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Layered Magnesium Diboride and its Derivatives as Potential Catalytic and Energetic Additives for Tuning the Exothermicity of Ammonium Perchlorate

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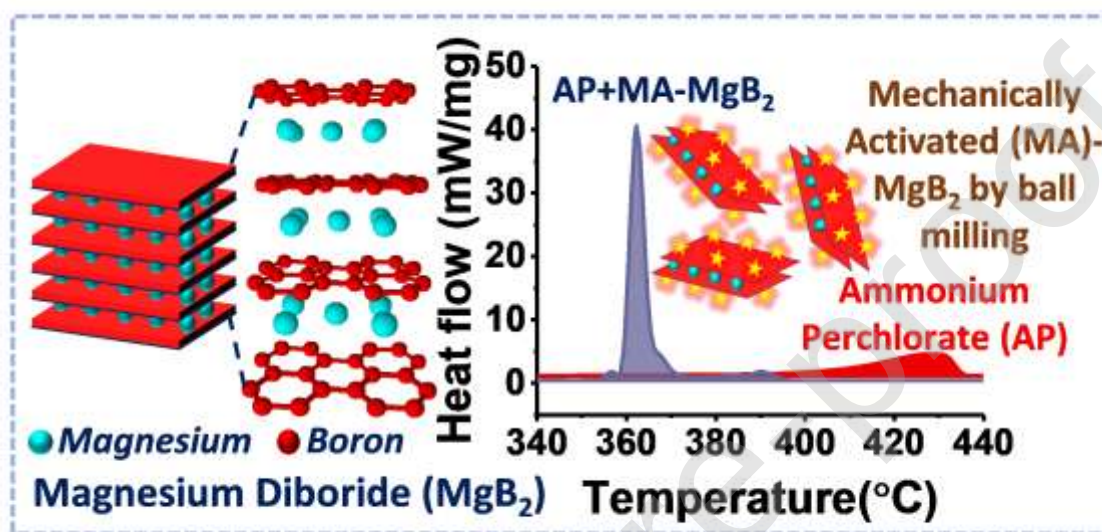
# Layered Magnesium Diboride and its Derivatives as Potential Catalytic and Energetic Additives for Tuning the Exothermicity of Ammonium Perchlorate

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## Graphical abstract



## Highlights

- Layered MgB<sub>2</sub> has the potential to serve as a catalytic and energetic fuel additive
- This potential can be further enhanced by activating MgB<sub>2</sub> using ball milling
- Adding 1wt. % ball-milled MgB<sub>2</sub> increases the energy of ammonium perchlorate by 78%
- Adding 1wt.% ball-milled MgB<sub>2</sub> reduces the decomposition by ~73°C
- The first study that utilizes MgB<sub>2</sub>, a conventional superconductor, as a fuel additive

## Abstract

In this article, we studied the effect of layered magnesium diboride (LMDB) and its micro and nano derivatives as catalytic and energetic additives towards the thermal decomposition of ammonium perchlorate (AP). We synthesized micro derivatives by mechanical activation of MgB<sub>2</sub> using ball milling and nano derivatives by dissolution recrystallization method. The mechanically activated MgB<sub>2</sub> (MA-MgB<sub>2</sub>) showed better performance than pristine MgB<sub>2</sub> (P-

MgB<sub>2</sub>) and boron-based nanosheets (NSs) on improving the thermal decomposition characteristics of AP. Addition of one wt. % of MA-MgB<sub>2</sub> to AP remarkably enhances the energy release by 78% and significantly reduces the decomposition temperature by ~73°C. Using the isoconversional method, we obtained activation energy, pre-exponential factor, and reaction model of AP and AP+1%MA-MgB<sub>2</sub>. The MA-MgB<sub>2</sub> performs much better than many other catalysts at similar loadings. This study provides a newer perspective to utilize the untapped potential of metal diborides and their derivatives for composite solid propellants.

**Keywords:** layered magnesium diboride, ammonium perchlorate, catalytic additive, and composite solid propellants

## 1. Introduction

Ammonium perchlorate (AP) is a widely used energetic material that acts as a strong oxidizer and facilitates self-sustained combustions [1]. It is a major ingredient in the currently used composite solid propellant fuels (CSPFs) and accounts for ~60-80% of the total weight of CSPFs [2–5]. The thermal decomposition characteristics of AP significantly affect the combustion performance of the propellant, which in turn determines the degree to which energy can be extracted [6]. To improve the thermal decomposition of AP, fuel additives and burn rate modifiers are incorporated in the fuel [7]. Generally, metals with a high heat of combustion are used as fuel additives [8,9]. Some energetic metal fuel additives include Li, Be, B, Si, Al, Mg, Ti, and Zr (heat of combustion values of energetic metals listed in Table S1, SI) [9,10]. Li and Be are not widely used because they are highly toxic and expensive [10,11]. Aluminum is the most commonly used metal fuel additive because of its wide availability, ease of handling, the high heat of combustion (31.4 MJ/kg), and also more economical [10,12].

On the other hand, several burn rate modifiers are added to AP to improve the burning rate of the propellant. The burn rate modifiers or combustion modifiers are classified as catalysts (increase the burning rate) and inhibitors (decrease the burning rate) based on their activity on the combustion performance of the propellant [13]. The burn rate modifiers include metals, metal oxides, and mixed metal oxides as they can exhibit variable oxidation states by forming complex molecules with the reagents [7,14–16]. The formed metal complex molecules can either donate or accept the electrons from the transition state of the reaction and facilitate the reaction to occur [14]. Conventionally, transition metal oxides (TMOs) have been used as catalysts, and some commonly used catalytic additives include Fe<sub>2</sub>O<sub>3</sub>, CuO, MnO<sub>2</sub>, Ni<sub>2</sub>O<sub>3</sub>, copper chromite, and SiO<sub>2</sub> [7,13,17–19]. LiF is reported as an inhibitor to the

decomposition reaction of AP, and it decreases the burn rate of the propellant by forming  $\text{NH}_4\text{F}$  through the formation of  $\text{LiF-NH}_4\text{ClO}_4$  eutectic mixture [13].

Boron is another universal fuel additive in propellants; it exhibits the highest theoretical heat of combustion in terms of both volumetric (135.8MJ/L), and gravimetric (58.5MJ/kg) terms. Its gravimetric heat of combustion is nearly double that of aluminum, and also greater than several other traditionally used metal fuel additives [20,21]. Yet, scientists are not able to effectively utilize the potential of boron because of the challenges associated with its combustion. The challenge is that upon combustion, boron forms a viscous boron oxide layer on the surface that limits further oxidation of boron [22,23]. Kuwahara et al. reported that increasing the surface area by nanoscaling/micro scaling the boron improves its combustion efficiency [24]. However, by reducing the particle size, it is not possible to completely overcome the problem of oxide layer passivation. Furthermore, at a small size scale, the problem of agglomeration increases. Moreover, the methods to obtain nanoforms of boron are not scalable [25–27]. Some studies have reported that the challenges associated with the combustion of boron can be overcome by surface modification and coating the individual particles with LiF, Viton A, and silane [28–31]. The alternative strategy that was recently reported to overcome the challenge is to add active metals to boron. Liu et al. investigated various ratios of Mg/B mixtures and shown that the addition of magnesium to boron improves the burning of boron particles [32]. Recently, metal borides are gaining renewed attention as alternative energetic materials to boron as fuel additives because of their high heat of combustion. Several researchers have begun investigating various methods to synthesize high-quality metal borides for solid propellant rocket engines [10,33–35].

In the past seven years, our research group has established the science of nanoscaling metal borides (MBs) of the form  $\text{MB}_2$  to obtain boron analogs of graphene. MBs of the form  $\text{MB}_2$  [36] consists of metal atoms sandwiched between covalently bonded hexagonal networks of boron (Figure 1). MBs are commonly used in steel hardening, turbine blades, corrosive resistant, and refractory coatings because of their excellent mechanical, chemical, and electrical properties [37]. Until our previous studies [38–42], they have never been probed as a potential candidate for yielding quasi-2D boron nanostructures. We had revisited the chemistry of a well-known layered material, magnesium diboride ( $\text{MgB}_2$ ), popularly known for its superconducting properties and had shown that it is possible to exfoliate  $\text{MgB}_2$  [38–42]. With a curiosity to understand the physico-chemical interaction between  $\text{MgB}_2$  and water, we had also discovered a simple and scalable recipe to obtain various quasi 2D boron-

based nanostructures in high-yield [40]. The quasi 2D boron-based nanostructures utilized in this study were synthesized using the recipe of dissolution-recrystallization method [40] discovered by us earlier.

In this article, we firstly showed the effect of quasi 2D boron-based nanostructures on thermal decomposition of AP. We then demonstrated that pristine  $\text{MgB}_2$  (P- $\text{MgB}_2$ ) is a potential catalytic and energetic additive for enhancing the thermal decomposition characteristics of AP. To further enhance the activity of P- $\text{MgB}_2$ , we prepared mechanically activated- $\text{MgB}_2$  (MA- $\text{MgB}_2$  or micro derivatives) by developing an optimized ball milling recipe (Fig.1). Finally, we show that the addition of one wt. percentage of MA- $\text{MgB}_2$  enhances the thermal decomposition of AP leading to an enhanced release of energy, better than several other existing catalysts. To the best of our knowledge, there are no existing reports on using  $\text{MgB}_2$  and its derivatives as additives for tuning the exothermicity of AP. This study provides a maiden insight on utilizing the layered magnesium diboride (LMDB) and its micro and nano derivatives as potential catalytic and energetic additives for future solid propellants.

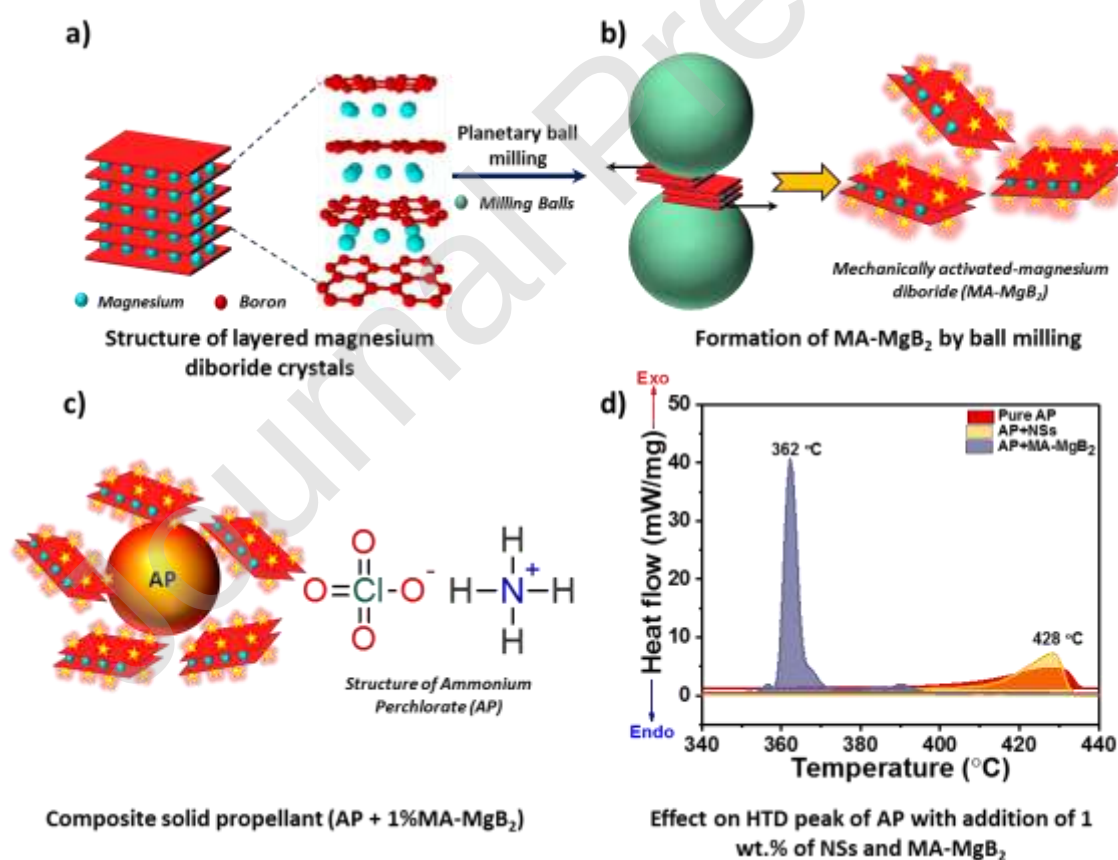


**Figure 1.** Schematic representing the formation of mechanically activated-magnesium diboride (MA-MgB<sub>2</sub>) using planetary ball milling. (a) structure of layered magnesium diboride (LMDB) representing the presence of magnesium atoms sandwiched between boron honeycomb planes, (b) planetary ball milling of MgB<sub>2</sub> crystals yields in the formation of MA-MgB<sub>2</sub>, (c) composite solid propellant containing AP and one wt. percentage of MA-MgB<sub>2</sub>, and (d) DSC curve showing the effect of one wt. % of boron-based Nanosheets (NSs) and MA-MgB<sub>2</sub> on the high temperature decomposition (HTD) peak of AP.

## 2. Materials and Methods

### 2.1 Reagents and Chemicals:

The received ammonium perchlorate ( $\text{NH}_4\text{ClO}_4$ ) has a mean particle size of  $\sim 300\ \mu\text{m}$ . Standard Magnesium diboride ( $\text{MgB}_2$ ) powder of -100-mesh size with  $\geq 99\%$  purity was purchased from Sigma–Aldrich and used as pristine- $\text{MgB}_2$  (P- $\text{MgB}_2$ ). Deionized (DI) water was used for the ultrasonication of  $\text{MgB}_2$ .

### 2.2 Micronization of Ammonium Perchlorate (AP):

AP particle size of  $\sim 30\ \mu\text{m}$  was prepared using a planetary ball mill (Insmart, India), processed for 35 min at 375 rpm with a 4:1 ball to powder ratio (zirconia ball diameter is  $\sim 10\ \text{mm}$ ). Further, various size particles were segregated by mesh sieving. The particle size analysis of micronized AP is shown in Fig. S1. With this milling parameters, we majorly obtained  $30\ \mu\text{m}$  size and a tiny fraction of  $16\ \mu\text{m}$  size AP particles. For all our studies, AP30 is only used, and until our further studies, the micronized AP particles are sealed tightly and stored under vacuum.

### 2.3 Synthesis of various boron-based nanostructures:

Various boron-based nanostructures (NS) were prepared using a sonication process according to the dissolution and recrystallization recipe showed in our previous work [40]. In brief, 3 mg/ml of P- $\text{MgB}_2$  in DI water was taken in a double-walled jacketed vessel at  $25^\circ\text{C}$ . The mixture is probe sonicated using a half-inch probe (Qsonica 500 W) with operating parameters: 30% amplitude and 10 seconds ON, 10 seconds OFF pulse for 30 minutes. The obtained dark suspension was left undisturbed for 24 hours and then vacuum filtered using  $0.22\ \mu\text{m}$  filter paper (Durapore GVWP 47 mm). The obtained golden yellow color filtrate was allowed to age for 0h, 24h, 48h, and 72h to get boron-based nanodots, nanograins, nanoflakes, and nanosheets respectively. The powder form of these boron-based nanostructures was obtained by lyophilizing the filtrate at the above specified aging times.

### 2.4 Preparation of mechanically activated- $\text{MgB}_2$ (MA- $\text{MgB}_2$ ):

The MA- $\text{MgB}_2$  were prepared by planetary dry ball milling (Insmart, India), of P- $\text{MgB}_2$ . A measured quantity of P- $\text{MgB}_2$  crystals was taken in a zirconia bowl (10 cm inner diameter) to which zirconia balls (6mm diameter) were added. The balls to powder ratio were maintained as 5:1 (w/w); a milling speed of 150 rpm was used, and the milling time varied from 2h to 30h. During milling, at specific time intervals (e.g., 2h, 4h, 6h, 17h, 25h, and 30h), a small amount of sample ( $\sim 1\ \text{gm.}$ ) was collected and stored in vacuum for further characterizations. The ball-

milling was performed with different cases to identify the optimal milling parameters. The various cases are as follows:

Case 1: Milling with 6 mm balls

Case 2: Milling with 10 mm balls

Case 3: Milling with 90% of 6 mm balls and 10% of 10 mm balls

Case 4: Milling with 80% of 10 mm balls and 20% of 6 mm balls

In all the cases, the milling speed is 150 rpm, ball to powder ratio is 5:1 (w/w), and by comparing the DSC studies of all milled samples for various cases, we found that milling with 6mm balls for 17h is effective in terms of energy release and in reducing the decomposition temperature. Therefore, all further characterizations were done on the MA-MgB<sub>2</sub> sample obtained after 17h of milling from case-1. The particle size analysis of the P-MgB<sub>2</sub> and MA-MgB<sub>2</sub> are shown in Fig. S2. With increasing milling time, the average particle of MgB<sub>2</sub> was found to be significantly decreased.

## 2.5 Preparation of composite solid propellant fuels (CSPFs):

The micronized AP (~30 µm) and P-MgB<sub>2</sub>/MA-MgB<sub>2</sub>/boron-based NSs were mixed in a regular mortar and pestle at a mass ratio of 99:1 to prepare the CSPF samples for thermal decomposition analysis. In general, ~1980 mg of micronized AP sample is mixed with ~20 mg (one wt. %) of P-MgB<sub>2</sub>/MA-MgB<sub>2</sub>/boron-based NSs in a mortar and pestle and gently mixed to obtain a uniform mixture. We also observed that the addition of P-MgB<sub>2</sub>/MA-MgB<sub>2</sub>/boron-based NSs improves the free-flowing nature of the micronized AP particles.

## 2.6 Activation energy using Kissinger-Akahira-Sunose (KAS) method:

To determine the activation energy, we followed Kissinger-Akahira-Sunose (KAS) method, a model free isoconversional integral method formulated for linear non-isothermal heating studies [43,44]. The KAS method is based on an approximation described by equation (1).

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) = \text{Constant} - \frac{E_\alpha}{RT_{\alpha,i}} \quad (1)$$

Where,

$\beta_i$  = i<sup>th</sup> heating rate

$T_{\alpha,i}$  = temperature at which the extent of conversion  $\alpha$  is reached under the i<sup>th</sup> heating rate

$E_\alpha$  = activation energy at the extent of conversion  $\alpha$ , and

$R$  = universal gas constant

A detailed derivation of the equation is shown in the kinetics section of the supporting information file. The extent of conversion or reacted fraction  $\alpha$ , as a function of time is obtained by equation (2).

$$\alpha(t) = \frac{m(i) - m(t)}{m(i) - m(f)} \quad (2)$$

Where  $m(i)$  is the initial mass,  $m(t)$  is the mass at any time  $t$ , and  $m(f)$  is the final mass obtained from TGA analysis. To use this method, we need to obtain TGA data for at least three different heating rates. We have performed the TGA analysis at the heating rates ( $\beta_i$ ) of 5, 10, 15, 20, and 25 K/min. By using equation (2), we determined the conversion  $\alpha(t)$  for each heating rate ( $\beta_i$ ) and plotted conversion  $\alpha(t)$  vs. temperature ( $T_{\alpha,i}$ ) for all the heating rates ( $\beta_i$ ). We then obtained the exact values of temperatures for discrete values of conversion ( $\alpha = 0.1$  to 0.9 with a step size of 0.05) by interpolating the data of conversion and temperature at each heating rate. For the conversion  $\alpha = 0.1$ , we noted the temperatures at the different heating rates  $\beta_1, \beta_2, \beta_3, \beta_4$ , and  $\beta_5$  as  $T_{\alpha,1}, T_{\alpha,2}, T_{\alpha,3}, T_{\alpha,4}$ , and  $T_{\alpha,5}$  respectively. Using the values of  $\beta_i$  and  $T_{\alpha,i}$ , we utilized the equation (1) and plotted  $\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right)$  vs.  $\frac{1}{T_{\alpha,i}}$  for the conversion  $\alpha = 0.1$  to obtain the value of activation energy ( $E_{\alpha=0.1}$ ) from the slope ( $-E_{\alpha}/R$ ) of the linear fit. By plotting  $\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right)$  vs.  $\frac{1}{T_{\alpha,i}}$  at each discrete value of conversion, we can obtain the values of activation energy ( $E_{\alpha}$ ) for each conversion. In this way, we obtained the plot of activation energy ( $E_{\alpha}$ ) vs. conversion ( $\alpha$ ) for the thermal decomposition of the composite solid propellant AP and AP+1%MA-MgB<sub>2</sub>. This plot is helpful to understand the decomposition behavior at various stages of conversion.

## 2.7 Master plots based on differential form of generalized kinetic equation to determine the reaction model:

Master plots are theoretical curves that depend on rate determining mechanism and are independent of reaction parameters [45]. We utilized the differential form of reaction models [ $f(\alpha)$ ] shown in Table 4, to obtain the theoretical master plot in differential form. The derivation for the equation of master plot is shown in supporting information file.

Generalized equations of differential form of master plot are as shown below:

$$\frac{d\alpha/d\theta}{(d\alpha/d\theta)_{\alpha=0.5}} = \frac{f(\alpha)}{f(0.5)} \quad (3)$$

$$\frac{d\alpha/d\theta}{(d\alpha/d\theta)_{\alpha=0.5}} = \frac{d\alpha/dt}{(d\alpha/dt)_{\alpha=0.5}} \frac{\exp(E/RT)}{\exp(E/RT_{0.5})} \quad (4)$$

Equation (3) represents that for a given value of  $\alpha$ , the experimentally determined value of reduced-generalized reaction rate  $\frac{d\alpha/d\theta}{(d\alpha/d\theta)_{\alpha=0.5}}$  corroborates with the theoretically calculated value of  $\frac{f(\alpha)}{f(0.5)}$  when an appropriate differential reaction model  $[f(\alpha)]$  is applied. Furthermore,  $f(0.5)$  is constant for a given reaction model shown in table 4. Plotting  $\frac{f(\alpha)}{f(0.5)}$  vs. conversion ( $\alpha$ ) gives the theoretical master plot, which is shown in Figure 8. From equation (4), the reduced-reaction rate  $\frac{d\alpha/d\theta}{(d\alpha/d\theta)_{\alpha=0.5}}$  can be obtained using the experimental data from TGA analysis recorded at a constant heating rate. The average activation energy value obtained from any of the model free isoconversional methods can be used. Comparing theoretical master plot with experimental reduced rate, we found the suitable match of reaction model of the sample.

## 2.8 Determination of pre-exponential factor (A)

After determining the suitable reaction model, we obtained the pre-exponential factor (A) using Coats-Redfern method, a well-known integral form of kinetic equation: [43]. The equation is as shown below:

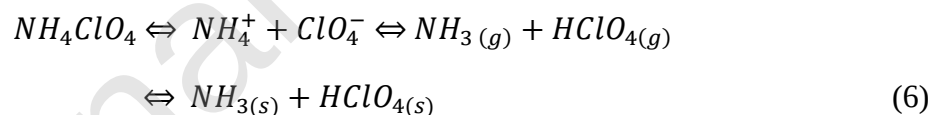
$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) = \ln\left(\frac{A_\alpha R}{g(\alpha)E_\alpha} \left[1 - \frac{2RT_{exp}}{E_\alpha}\right]\right) - \frac{E_\alpha}{RT_{\alpha,i}} \quad (5)$$

Where,  $\beta_i$  is the heating rate, and  $T_{\alpha,i}$  is the temperature for an  $i^{\text{th}}$  heating rate at a particular conversion  $\alpha$ . This equation is similar to KAS equation shown in equation (1). So plotting  $\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right)$  vs.  $\frac{1}{T_{\alpha,i}}$  as explained earlier, we obtained the slope and intercept. From the intercept, using the integral form of the reaction model  $g(\alpha)$  determined from the master plot curve, we obtained pre-exponential factor ( $A_\alpha$ ). Here,  $T_{exp}$  is the mean temperature calculated from the temperature values recorded for different heating rates for a particular value of conversion. In

this way, we obtained pre-exponential factor at each discrete value of conversion. And the constable plot of  $\ln A$  vs.  $E_a$  fitting to a straight line shows the kinetic compensation effect at every stage of conversion. From the obtained kinetic triplets ( $E$ ,  $A$ , reaction model), we can provide the complete reaction rate for the thermal behavior of a solid material.

## Results and discussions

The quasi 2D boron-based nanostructures were obtained by dissolution and recrystallization of  $MgB_2$  crystals (Fig. 1a) in water using the protocol described in our previous work (brief about synthesis in the methods section) [40]. The morphology of the P- $MgB_2$  and the quasi 2D boron-based nanostructures (nanodots (NDs), nanograins (NGs), and nanosheets (NSs)) are shown in Fig. S3. To see the effect of these boron-based nanostructures on thermal decomposition of AP, we have performed the simultaneous thermal analysis (preparation of AP and its composites (CSPFs) in the methods section). Fig. 2a shows the differential scanning calorimetry (DSC) graph of pure AP or with no additive, which typically indicates one endothermic peak at 245 °C corresponding to the solid-state phase transition from orthorhombic to cubic phase [2]. The other two exothermic peaks in the range of 270 to 440 °C correspond to the decomposition peaks of AP. The small exothermic peak at 283 °C corresponds to low-temperature decomposition (LTD) resulting from the partial decomposition of AP, and the higher exothermic peak at 428 °C, which is attributed to the complete decomposition, is known as high-temperature decomposition (HTD) peak [46]. In general, the thermal decomposition reaction of AP is described as follows [2]:



The two-stage thermal decomposition of pure AP was also verified through thermogravimetric analysis (TGA). Fig. 2b shows the mass loss of pure AP; at LTD and HTD, the mass loss corresponds to 24% and 75%, respectively. The detailed information of AP decomposition data is summarized in Table 1. Fig. 2a shows the DSC curves of AP decomposition in the presence of one wt. percentage of boron-based nanosheets (NSs); Fig. S4 shows these curves in the presence of NDs and NGs. With the addition of one wt. percentage of boron-based nanostructures (i.e., either NDs/NGs/NSs) to AP, we observed a right shift of ~20 °C in the LTD peak of AP and no change in either phase transition peak or HTD peak as per DSC analysis. This signifies that the initiation of AP decomposition is delayed with the addition of boron-based nanostructures. This is probably due to the presence of functional

groups on the nanostructures [40], which is evident from the FTIR data shown in Fig. S5. These boron-based nanostructures were found to be functionalized with chemical functions such as hydrides, oxides, and hydroxide functional groups, which might be hindering the LTD process of AP [2]. This is also evident from the TGA mass loss curves as we can observe a slight deviation at both the stages of mass loss as compared to pure AP (Fig. 2b and S4). We observed clear shifts in the decomposition peaks of AP and its composites in the DTG plots. The effect of NSs as additives on thermal decomposition of AP is shown in Fig 2, and the effect of NDs and NGs are shown in Figure S4. We observed that LTD peak is right shifted in the presence of nanostructures. However, while the position of HTD peak for AP does not change in presence of NDs and NGs but it is significantly left shifted in presence of NSs. This suggests that the presence of boron-based nanostructures hinders only LTD and promotes HTD, which is clearly evident from the DTG plot shown in Fig. 2d in the presence of NSs. We also observe an increase in the exothermicity of AP from 763 J/g to 1094 J/g (Fig. 3a and Table 1), i.e., a ~40% increase in the energy release of AP in the presence of boron-based nanosheets. To verify this, we have performed the hyphenated TGA-mass spectrometry (MS) of gas residues produced that will demonstrate later the boron gaseous species released during the HTD process.

To obtain more insights into the performance of these boron-based nanostructures derived from LMDB, we also conducted control experiments with the parent material, P-MgB<sub>2</sub> as an additive in AP decomposition. Surprisingly, we found a significant enhancement in the decomposition characteristics of AP in the presence of P-MgB<sub>2</sub>. We noticed a sharp rise in the HTD peak of AP along with a shift towards lower temperature. Almost no changes in the phase transition and LTD peaks were observed in the case of P-MgB<sub>2</sub>. We observed that the HTD of AP is significantly promoted, just by an addition of one wt. % of P-MgB<sub>2</sub> (Fig. 2a). We noticed a left shift of ~62°C in HTD peak of AP along with an increase in the exothermicity of AP from 763 J/g to 1239 J/g (Fig. 3a and Table 1), i.e., a ~62% increase in the energy release of AP in the presence of P-MgB<sub>2</sub>. This unprecedented increase in exothermicity and decrease in decomposition temperature of AP can be attributed to the combined effect of presence of magnesium metal atoms (as catalyst) and boron planes (as fuel additive) together in the P-MgB<sub>2</sub>. This indicates that P-MgB<sub>2</sub> acts as a catalytic as well as energetic additive towards the thermal decomposition of AP. To the best of our knowledge, there are no existing reports, which study the effect of MgB<sub>2</sub> as an additive on thermal decomposition characteristics of AP. Motivated by the superior performance exhibited by MgB<sub>2</sub>, we endeavored to develop a way to nanoscale MgB<sub>2</sub> with minimal or no functionalization, as nanomaterials are expected to

show a superior activity than their parent material [47]. Based on the knowledge obtained from our previous studies on exfoliating  $\text{MgB}_2$  [38–42], we know that liquid phase exfoliation yields in the functionalized form of boron-based nanosheets. So, here we decided to use the dry ball milling method [48] to nanoscale  $\text{MgB}_2$  as this method is easily scalable and is used to obtain pristine or minimally functionalized nanosheets from other layered materials.

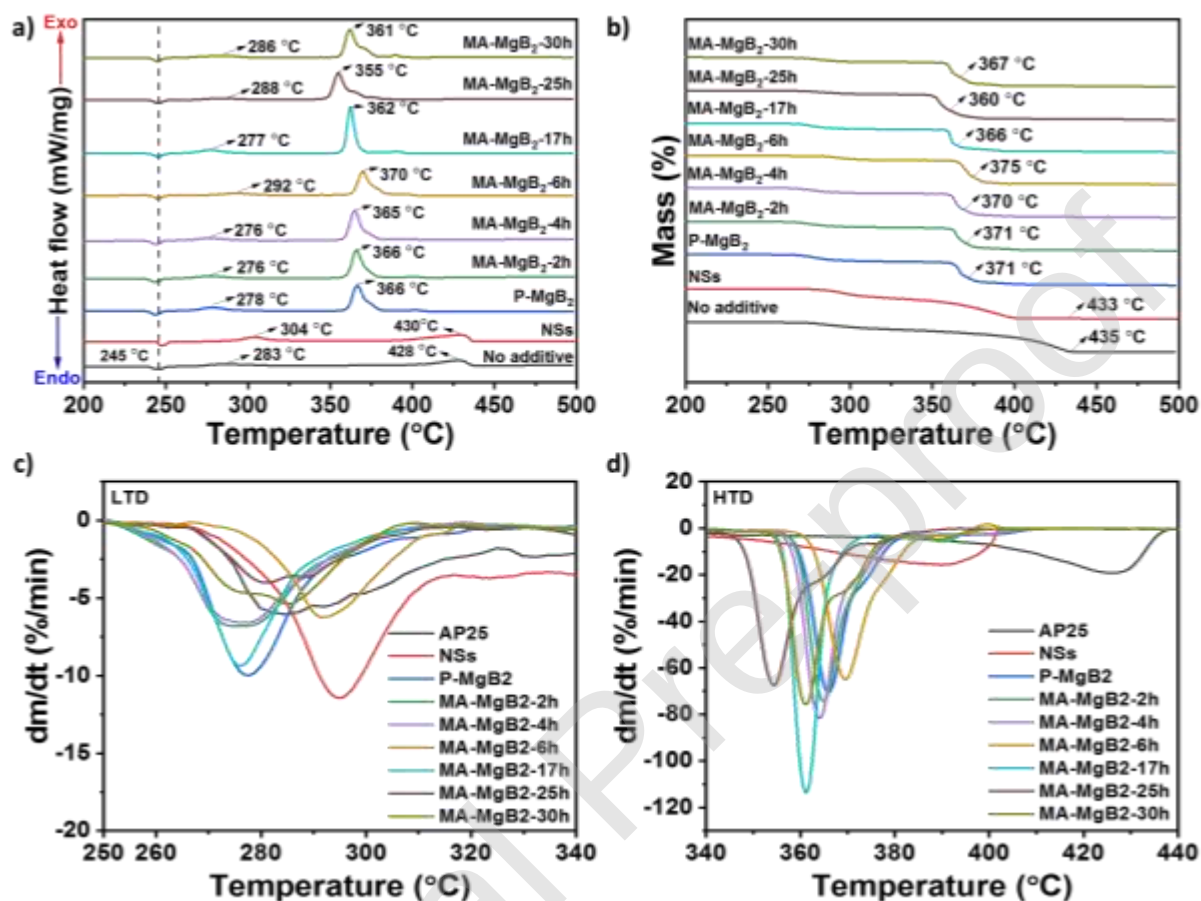


**Figure 2.** (a) DSC curves, (b) TGA curves, and (c), (d) DTG curves for the LTD and HTD of AP decomposition in the absence and presence of additives derived from LMDB at a 1% mass basis — No additive or Pure AP, Nanosheets (NSs), Pristine (P)- $\text{MgB}_2$ , Mechanically Activated (MA)- $\text{MgB}_2$ -2h, MA- $\text{MgB}_2$ -4h, MA- $\text{MgB}_2$ -6h, MA- $\text{MgB}_2$ -17h, MA- $\text{MgB}_2$ -25h, and MA- $\text{MgB}_2$ -30h, respectively. Among all, the presence of MA- $\text{MgB}_2$ -17h significantly increased the intensity of the HTD peak of AP along with increased energy release and decreased decomposition temperature.

In this pursuit, we identified an optimized set of milling parameters such as milling speed, milling time, ball diameter, and ball to powder ratio. During milling, the balls have an impact of compressive and shear forces on the milling material. If compressive forces dominate, then it results in more fragmentation of the material while shear force dominant milling results in exfoliation of layered material. Li et al. have shown that milling of bulk h-

BN at low speeds results in shear force dominant milling and produces a high yield of h-BN nanosheets [49]. Considering these facts, we designed four cases of ball milling to identify the optimum milling parameters, such as ball diameter and milling time. We fixed the milling speed as 150 rpm (low milling speed for shear force dominance) and ball to powder ratio as 5:1 (w/w) and performed the milling of P-MgB<sub>2</sub> for all the four cases. The milled samples were collected at different time intervals (0, 2, 4, 6, 17, 25, and 30h) for all the four cases and subsequently used to prepare the composites of AP. We performed the DSC analysis of all the composites (Tables S2-S5). We found that milling with 6 mm balls has shown better performance and we also have observed a gradual improvement in performance with increasing the milling time, as shown in Fig 2. Therefore, further analysis was done on the milled MgB<sub>2</sub> samples obtained from milling with 6 mm balls. From here, we termed the milled samples as mechanically activated-MgB<sub>2</sub> (MA-MgB<sub>2</sub>).

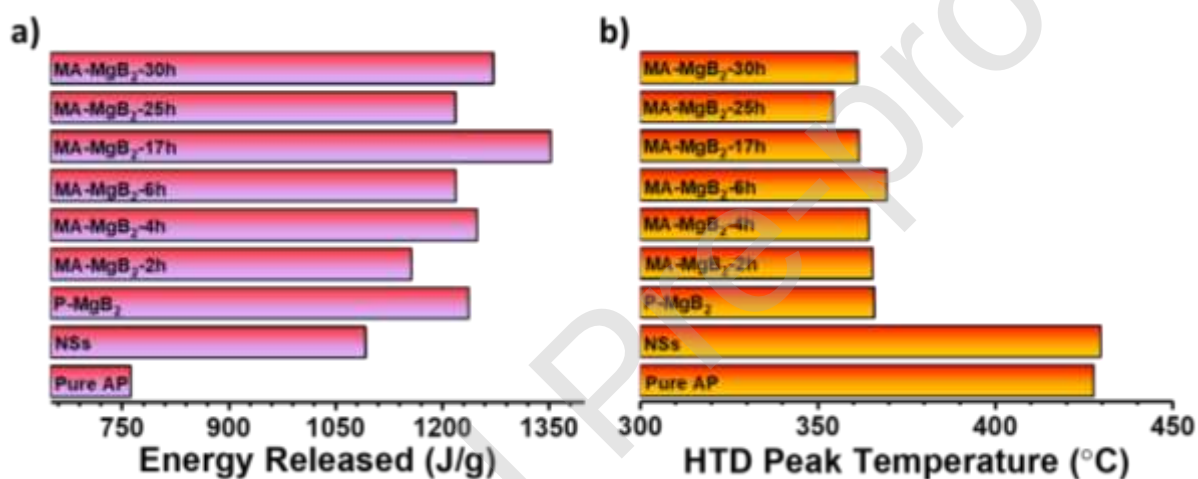


**Figure 3.** (a) Energy released and (b) HTD peak temperature of the AP decomposition in the absence and presence of additives derived from LMDB at a 1% mass basis — No additive or Pure AP, Nanosheets (NSs), Pristine (P)-MgB<sub>2</sub>, Mechanically Activated (MA)-MgB<sub>2</sub>-2h, MA-MgB<sub>2</sub>-4h, MA-MgB<sub>2</sub>-6h, MA-MgB<sub>2</sub>-17h, MA-MgB<sub>2</sub>-25h, and MA-MgB<sub>2</sub>-30h, respectively. In the presence of MA-MgB<sub>2</sub>-17h, the energy released is the highest with 1355 J/g along with a significant reduction in HTD peak temperature.

**Table 1.** Results of thermal decomposition of AP in the absence and presence of one wt. % of additives derived from LMDB at a heating rate of 10 K/min

| Composite | Peak        | End            | Mass loss | The energy released  |
|-----------|-------------|----------------|-----------|----------------------|
|           | Temperature | decomposition  |           |                      |
|           | Tm/°C       | temperature/°C | Δm/%      | ΔH/J g <sup>-1</sup> |

|                          | LTD | HTD |     | $\Delta m1$ | $\Delta m2$ |      |
|--------------------------|-----|-----|-----|-------------|-------------|------|
| No additive              | 283 | 428 | 435 | 24          | 75          | 763  |
| F-B-NDs                  | 305 | 431 | 433 | 28          | 71          | 1050 |
| F-B-NGs                  | 306 | 429 | 432 | 26          | 73          | 1061 |
| F-B-NSs                  | 304 | 430 | 433 | 27          | 72          | 1094 |
| P-MgB <sub>2</sub>       | 278 | 366 | 371 | -           | 100         | 1239 |
| MA-MgB <sub>2</sub> -2h  | 276 | 366 | 371 | -           | 96          | 1158 |
| MA-MgB <sub>2</sub> -4h  | 276 | 365 | 370 | -           | 96          | 1251 |
| MA-MgB <sub>2</sub> -6h  | 292 | 370 | 375 | -           | 95          | 1221 |
| MA-MgB <sub>2</sub> -17h | 277 | 362 | 366 | -           | 93          | 1355 |
| MA-MgB <sub>2</sub> -25h | 288 | 355 | 360 | -           | 98          | 1221 |
| MA-MgB <sub>2</sub> -30h | 286 | 361 | 367 | -           | 96          | 1274 |

To investigate the degree of exfoliation upon milling, we collected the powder X-ray diffraction (XRD) patterns of the samples obtained at different milling times (Fig. 4a). The XRD spectra of the P-MgB<sub>2</sub> crystals and the 2 h, 4 h, 6 h, 17 h, 25 h, and 30 h milled samples are compared in Fig. 4a to see the changes in peak intensities and positions. It can be seen that with an increase in the milling time, the peaks exhibit a slight reduction in the intensity and no shift in the peak positions were observed. In a crystal structure, the multiples of (001) plane correspond to the stacking of layers in c-direction, and the (hk0) planes represent the order within the basal sheets [50]. Therefore, to view the effect of milling on c-direction planes of LMDB, we compared the enlarged XRD spectra of (001) and (002) peaks corresponding to the P-MgB<sub>2</sub> and MA-MgB<sub>2</sub>-17h (Fig. 4b). It can be seen that even after 17 h of milling, no significant reduction in the intensity of both (001) and (002) peaks was observed. This is indicating that exfoliation has not occurred and resulted in the formation of MA-MgB<sub>2</sub> crystals. Extending the milling time further has an inverse effect of milling, which can be evident from the slight increase in the intensity of (001) peak for 25h and 30h milled samples in comparison with 17h milled sample (Fig. S6).

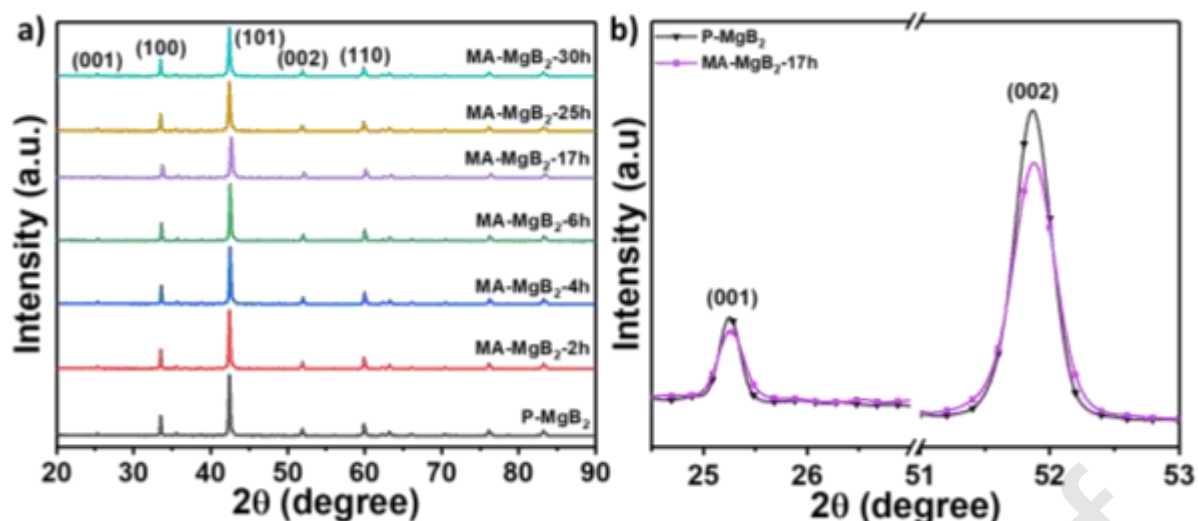


**Figure 4.** XRD analysis of (a) Pristine (P)-MgB<sub>2</sub> compared with Mechanically Activated (MA)-MgB<sub>2</sub> obtained at different milling times; (b) the enlarged spectra of (001) and (002) peaks corresponding to P-MgB<sub>2</sub> and the MA-MgB<sub>2</sub>-17h. With increasing the milling time, the P-MgB<sub>2</sub> did not result in significant exfoliation but yielded in the mechanical activation of MgB<sub>2</sub>.

Therefore, we acknowledge the fact that dry ball milling did not yield in exfoliation. However, the MA-MgB<sub>2</sub> as an additive shows superior activity than P-MgB<sub>2</sub> in enhancing the thermal decomposition of AP. Fig. 2a shows the decomposition of AP in the presence of one wt. percentage of MA-MgB<sub>2</sub> obtained at various milling times. We found that MA-MgB<sub>2</sub> obtained by 17 h of milling, enhances the exothermicity of AP in an excellent way better than many other existing catalysts (comparison with other catalytic additives is shown in Table 2). This remarkable catalytic activity is due to the presence of high-energy material boron (present along with the metal atom Mg), combined with the fact that this construct is available in a layered form that allows enhanced access to the active sites. This is of immense prospect for utilizing in the practical applications of missile fuels. We also determined the net amount of heat released in each case, and it was found to be 763, 1239, and 1355 J/g for pure AP and composites of AP with P-MgB<sub>2</sub> and MA-MgB<sub>2</sub>-17h samples respectively. The energy released data for the remaining samples are tabulated in table 1. This shows that we can enhance the decomposition energy of AP by ~78% just by adding one wt. percentage of MA-MgB<sub>2</sub>-17h. In addition to the increase of net heat released, we are also able to lower the temperature of complete decomposition peak (HTD peak) from 428 °C to 362 °C, a decrease of 66°C (Fig. 3b and Table 1). This suggests that MA-MgB<sub>2</sub>-17h acts as a catalytic and energetic additive in the thermal decomposition of AP. Hence, further studies were performed on MA-MgB<sub>2</sub> obtained at 17 h of milling, and from here, we term it as MA-MgB<sub>2</sub>.

**Table 2.** Comparison of catalytic and energetic activity for AP composites in the presence of various additives that are reported in the literature

| Additive                                 | Loadin<br>g/wt. % | Enhancement<br>in energy<br>release/% | The shift in<br>HTD peak<br>temperature/°C | Reference          |
|------------------------------------------|-------------------|---------------------------------------|--------------------------------------------|--------------------|
| <b>P-MgB<sub>2</sub></b>                 | <b>1</b>          | <b>+62</b>                            | <b>-62</b>                                 | <b>This work</b>   |
| <b>MA-MgB<sub>2</sub>-17h</b>            | <b>1</b>          | <b>+78</b>                            | <b>-66</b>                                 | <b>This work</b>   |
| <b>MA-MgB<sub>2</sub>-25h</b>            | <b>1</b>          | <b>+60</b>                            | <b>-73</b>                                 | <b>This work</b>   |
| Cu@h-BN                                  | 2                 | +36                                   | -45                                        | Huang et al.[51]   |
| GO                                       | 2                 | -                                     | -32                                        | Memon et al.[52]   |
| Al (25 nm)                               | 5                 | -31                                   | -8                                         | Liu et al.[53]     |
| Anatase TiO <sub>2</sub>                 | 1                 | +69                                   | -30                                        | Reid et al.[54]    |
| TiO <sub>2</sub> (20 nm)                 | 1                 | -10                                   | +6                                         | Dixit et al.[55]   |
| Fe <sub>2</sub> O <sub>3</sub> (< 40 nm) | 1                 | +18                                   | +6                                         | Dixit et al.[55]   |
| SiO <sub>2</sub>                         | 1                 | +5                                    | -2                                         | Dixit et al.[55]   |
| CuO-h-BN                                 | 3                 | -                                     | -50                                        | Paulose et al.[56] |

The decomposition of AP in the presence of P-MgB<sub>2</sub> and MA-MgB<sub>2</sub> as a catalytic additive was further investigated by thermogravimetric analysis (TGA), as shown in Fig. 2b and Table 1. With the addition of one wt. percentage of P-MgB<sub>2</sub> or MA-MgB<sub>2</sub> milled samples to AP, we observe a significant reduction in the end decomposition temperature of AP. The shift in the LTD and HTD peaks can be noticed clearly from the DTG plots shown in Fig. 2c and 2d. The MA-MgB<sub>2</sub> sample shows remarkable catalytic activity by shifting the end decomposition temperature of AP from 435 °C to 366 °C (see Table 1). Compared with pure AP, there is a steeper decline in the TGA curves of samples with P-MgB<sub>2</sub> as well as with MA-MgB<sub>2</sub> samples. This again suggests that MgB<sub>2</sub> and its derivatives are excellent catalytic additives for thermal decomposition of AP.

To re-confirm the catalytic activity of MA-MgB<sub>2</sub> on the thermal decomposition reaction of AP, we need to know the kinetic triplets (activation energy, pre-exponential factor, and reaction model) for the thermal decomposition reaction of AP in the presence and absence of additives. So we have performed TGA-DSC studies of the AP and AP/MA-MgB<sub>2</sub> composites at different heating rates of 5, 10, 15, 20, and 25 K/min. It is known that the thermal decomposition of solid propellants is a multi-step process, and the reaction mechanism changes

with variation in temperature, and thus the activation energy of the system varies [57]. The temperature of decomposition and the heat release are highly dependent on the heating rate [58]. Fig. 5a and 5b, shows the DSC curves of pure AP and AP+1%MA-MgB<sub>2</sub> at different heating rates, indicating the shift in decomposition peaks to higher temperatures with increase in heating rate. All these measurements were recorded in an aluminum pan closed with a pierced lid under nitrogen as purge gas with a flow rate of 80 ml/min. From the TGA data obtained at each heating rate, we have calculated the extent of conversion ( $\alpha$ ) using equation (2). Fig. 5c and 5d shows the conversion ( $\alpha$ ) vs. temperature plot of pure AP and AP+1% MA-MgB<sub>2</sub> at heating rates of 5, 10, 15, 20, and 25 K/min. The curves of different heating rates are parallel to each other and indicating the delay in conversion with increase in heating rate.

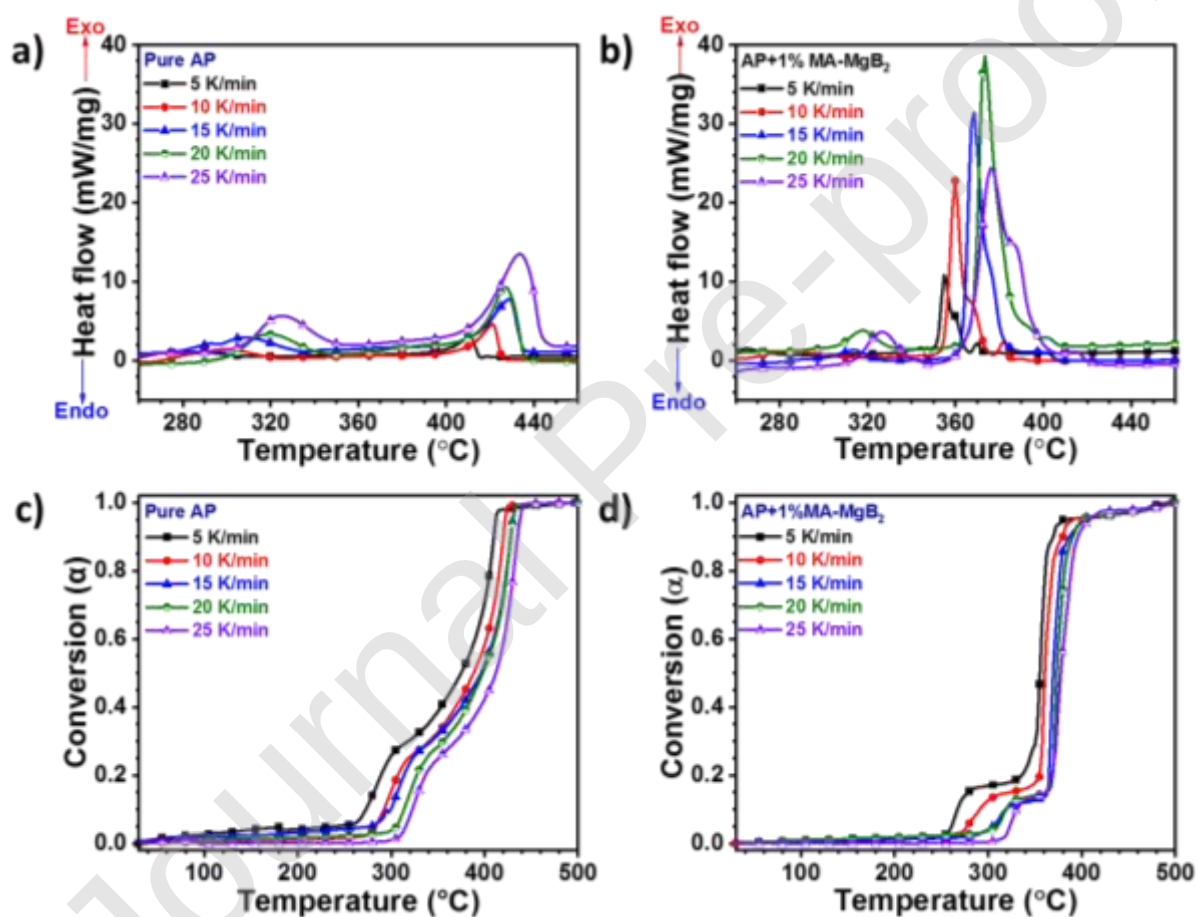


**Figure 5.** DSC curves and Conversion ( $\alpha$ ) vs. temperature plots for the thermal decomposition of (a), (c) pure AP; and (b) (d) AP+1% Mechanically Activated (MA)-MgB<sub>2</sub>. These plots were obtained at different heating rates: 5, 10, 15, 20, and 25 K/min in aluminum pan closed with a pierced lid; the measurements were made in a nitrogen environment (flow rate of 80 ml/min).

To understand the effect of MA-MgB<sub>2</sub>, we have shown the plots of  $\alpha$  vs. T for AP decomposition with and without additives at each heating rate in Fig. 6. From the plots shown in Fig. 6, we can clearly distinguish that in the presence of MA-MgB<sub>2</sub>, the curve is highly steep and the complete conversion is attained quickly at lower temperatures compared to pure AP. We provide a comparison (table 3) to see the difference in conversion at different temperature ranges for pure AP and AP+1% MA-MgB<sub>2</sub> at 5 K/min. From Table 3, we can find that at temperatures < 330°C, the conversion is very low and pure AP performs better than the presence of MA-MgB<sub>2</sub>. But from 330-380°C, the conversion spikes up suddenly from 0.19 to 0.95 in the presence of MA-MgB<sub>2</sub> whereas pure AP exhibits a conversion only from 0.3 to 0.5. This indicates that while pure AP decomposes 50%, the AP with one wt. % MA-MgB<sub>2</sub> achieves 95% decomposition, which indicates the merit of using MA-MgB<sub>2</sub> as an additive to CSPFs like AP. Decomposition of last 5% of the material is very slow and requires high temperatures; this additive appears to have no effect in the conversion range of 0.96-0.99.

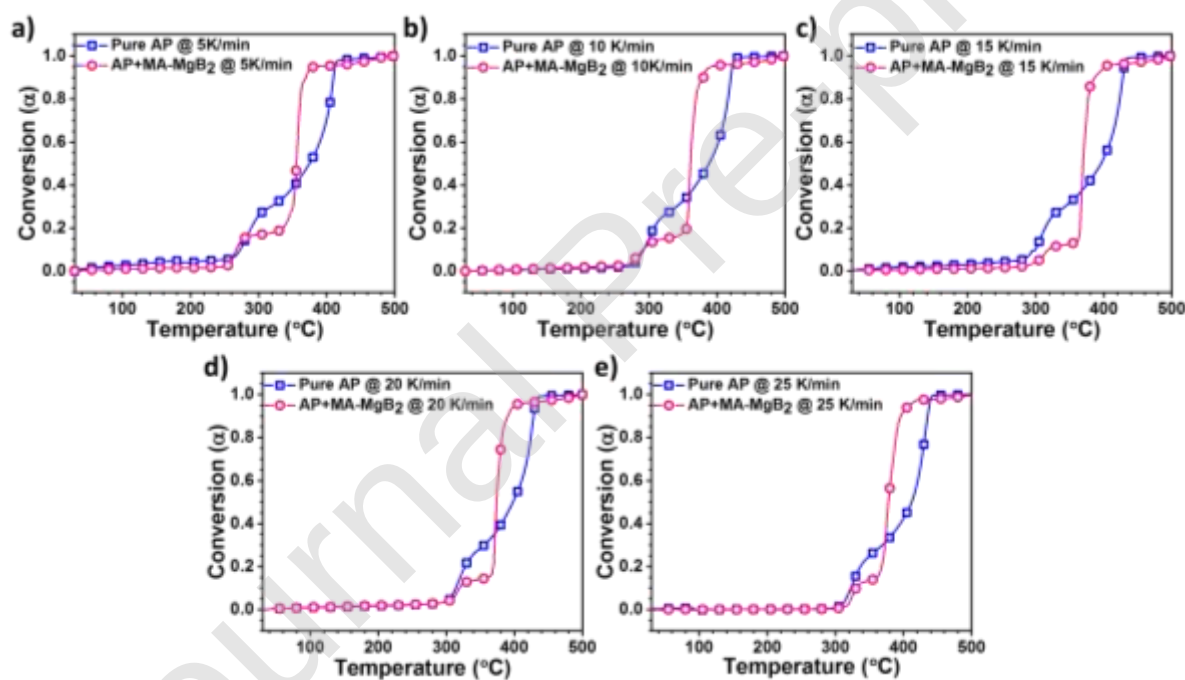


**Figure 6.** Conversion ( $\alpha$ ) vs. temperature plots for pure AP and AP+1%MA-MgB<sub>2</sub> at different heating rates: (a) 5 K/min, (b) 10 K/min, (c) 15 K/min, (d) 20 k/min, and (e) 25 K/min. The measurements were made in an aluminum pan closed with pierced lid under a nitrogen environment (flow rate of 80 ml/min).

**Table 3.** Comparison of conversion of thermal decomposition of AP in the absence and presence of 1% MA-MgB<sub>2</sub> at 5 K/min

| Temperature range (°C) | Conversion ( $\alpha$ ) |                           |
|------------------------|-------------------------|---------------------------|
|                        | Pure AP                 | AP+1% MA-MgB <sub>2</sub> |
| 30-250                 | < 0.05                  | < 0.02                    |
| 250-280                | 0.05-0.14               | 0.02-0.15                 |
| 280-330                | 0.14-0.30               | 0.15-0.19                 |
| 330-380                | 0.30-0.50               | 0.19-0.95                 |
| 380-412                | 0.50-0.96               | 0.95-0.96                 |
| 412-480                | 0.96-0.99               | 0.96-0.99                 |

Now by using the conversion ( $\alpha$ ) vs. temperature data of different heating rates, we can find the first kinetic triplet–activation energy ( $E_\alpha$ ) at various stages of conversion.  $E_\alpha$ , at each conversion is obtained using an integral model free isoconversional method, Kissinger-Akahira-Sunose (KAS) method (the data processing is explained in the section 2.6). Following the KAS method, we obtained the activation energies of decomposition process with extent of conversion for the pure AP and AP+1%MA-MgB<sub>2</sub> and the respective curves with error bars are shown in Figure 7.

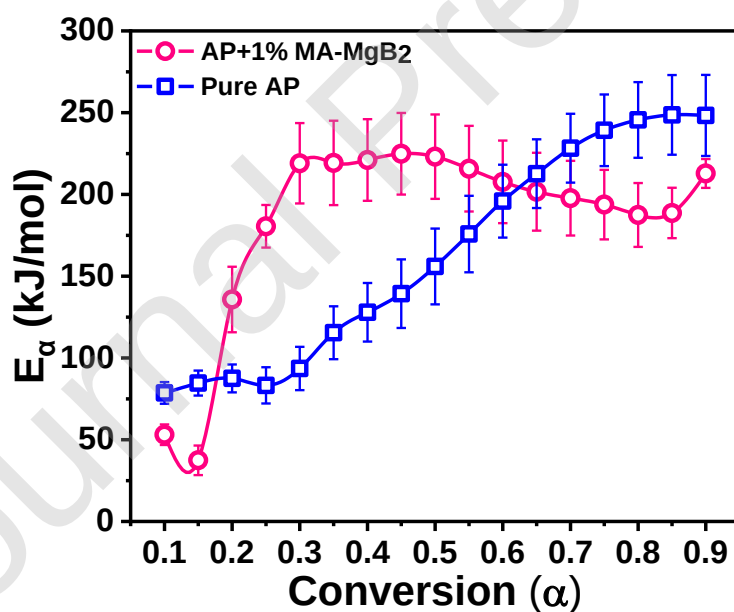


**Figure 7.** Activation energy ( $E_\alpha$ ) at discrete values of conversion obtained by Kissinger-Akahira-Sunose (KAS) method, an integral model free isoconversional approach. The catalytic behavior of MA-MgB<sub>2</sub> on thermal decomposition of AP is observed at lower ( $\alpha < 0.2$ ) and higher ( $\alpha > 0.6$ ) conversions. The activation energy curves of pure AP and AP+1% MA-MgB<sub>2</sub>

follow different paths with increase in conversion, suggesting completely different thermal behaviors.

From Fig. 7, it is evident that the decomposition of AP and its composite is not a single step process as the activation energy is varying throughout the process of decomposition. Comparison of  $E_a$  vs.  $\alpha$  curves for pure AP and AP+1% MA-MgB<sub>2</sub>, suggests that the thermal decomposition in both the cases follows entirely different paths indicating distinct thermal behaviors. For the case of pure AP, the activation energy varies from ~78 to 248 kJ/mol whereas for the case of AP+1% MA-MgB<sub>2</sub>, the activation energy varies from ~53 to 212 kJ/mol. Activation energy values are highly dependent on particle size, heating rate, purge gas flow rate, and open/closed lid while performing the decomposition studies of AP. So direct comparison with the available literature is not appropriate. Mallick *et al.* have recently studied the thermal decomposition kinetics of pure AP and also provided a comparative plot of activation energy vs. conversion of AP from various studies [6]. Among all the studies, the decomposition behavior of AP ( $E_a$  vs.  $\alpha$ ) observed by Zhu *et al.* [59] looks similar to the decomposition behavior of our AP+1%MA-MgB<sub>2</sub>. And the decomposition behavior of AP ( $E_a$  vs.  $\alpha$ ) observed by Vyazovkin looks similar to our case of pure AP [60,61]. Overall, we can comment that at lower ( $\alpha < 0.2$ ) and higher ( $\alpha > 0.6$ ) conversions, the catalytic behavior of MA-MgB<sub>2</sub> on thermal decomposition of AP is observed. Further, to determine the second kinetic triplet–pre-exponential factor (A), we need to first find the reaction model. The reaction model describes the rate determining mechanism of the reaction. Using the master plots we can find the reaction model (details explained in section 2.7). Fig. 8 shows the theoretical master plot  $\frac{f(\alpha)}{f(0.5)}$  vs. conversion ( $\alpha$ ) of various solid-state reaction mechanisms listed in Table 4.

**Table 4.** Reaction models of most common reaction mechanisms in solid-state reactions [6,45,61–63]

| S. No | Reaction Model                             | Model code | $f(\alpha)$                                      | $g(\alpha)$                         |
|-------|--------------------------------------------|------------|--------------------------------------------------|-------------------------------------|
| 1     | Power law                                  | P2         | $2\alpha^{\frac{1}{2}}$                          | $\alpha^{\frac{1}{2}}$              |
| 2     | Power law                                  | P3         | $3\alpha^{\frac{2}{3}}$                          | $\alpha^{\frac{1}{3}}$              |
| 3     | Power law                                  | P4         | $4\alpha^{\frac{3}{4}}$                          | $\alpha^{\frac{1}{4}}$              |
| 4     | Avrami-Erofeev: Tow-dimensional nucleation | A2         | $2(1 - \alpha)[- \ln(1 - \alpha)]^{\frac{1}{2}}$ | $[- \ln(1 - \alpha)]^{\frac{1}{2}}$ |

|    |                                                               |    |                                                                          |                                                                 |
|----|---------------------------------------------------------------|----|--------------------------------------------------------------------------|-----------------------------------------------------------------|
| 5  | Avrami-Erofeev: Three-dimensional nucleation                  | A3 | $3(1-\alpha)[- \ln(1-\alpha)]^{\frac{2}{3}}$                             | $[- \ln(1-\alpha)]^{\frac{1}{3}}$                               |
| 6  | Avrami-Erofeev: Four-dimensional nucleation                   | A4 | $4(1-\alpha)[- \ln(1-\alpha)]^{\frac{3}{4}}$                             | $[- \ln(1-\alpha)]^{\frac{1}{4}}$                               |
| 7  | Contracting cylinder: Two-dimensional phase boundary reaction | R2 | $2(1-\alpha)^{\frac{1}{2}}$                                              | $1 - (1-\alpha)^{\frac{1}{2}}$                                  |
| 8  | Contracting Sphere: Three-dimensional phase boundary reaction | R3 | $3(1-\alpha)^{\frac{2}{3}}$                                              | $1 - (1-\alpha)^{\frac{1}{3}}$                                  |
| 9  | Two-dimensional diffusion                                     | D2 | $[- \ln(1-\alpha)]^{-1}$                                                 | $(1-\alpha) \ln(1-\alpha) + \alpha$                             |
| 10 | Three-dimensional diffusion                                   | D3 | $\frac{3}{2}(1-\alpha)^{\frac{2}{3}}[1 - (1-\alpha)^{\frac{1}{3}}]^{-1}$ | $[1 - (1-\alpha)^{\frac{1}{3}}]^2$                              |
| 11 | Mampel (First order)                                          | F1 | $1-\alpha$                                                               | $-\ln(1-\alpha)$                                                |
| 12 | One-dimensional diffusion                                     | D1 | $\frac{1}{2}\alpha^{-1}$                                                 | $\alpha^2$                                                      |
| 13 | Ginstling-Brounstein                                          | D4 | $\frac{3}{2}\left((1-\alpha)^{-\frac{1}{3}} - 1\right)^{-1}$             | $1 - \left(\frac{2\alpha}{3}\right) - (1-\alpha)^{\frac{2}{3}}$ |
| 14 | Second order                                                  | F2 | $(1-\alpha)^2$                                                           | $(1-\alpha)^{-1} - 1$                                           |
| 15 | Third order                                                   | F3 | $(1-\alpha)^3$                                                           | $\frac{[(1-\alpha)^{-1} - 1]}{2}$                               |

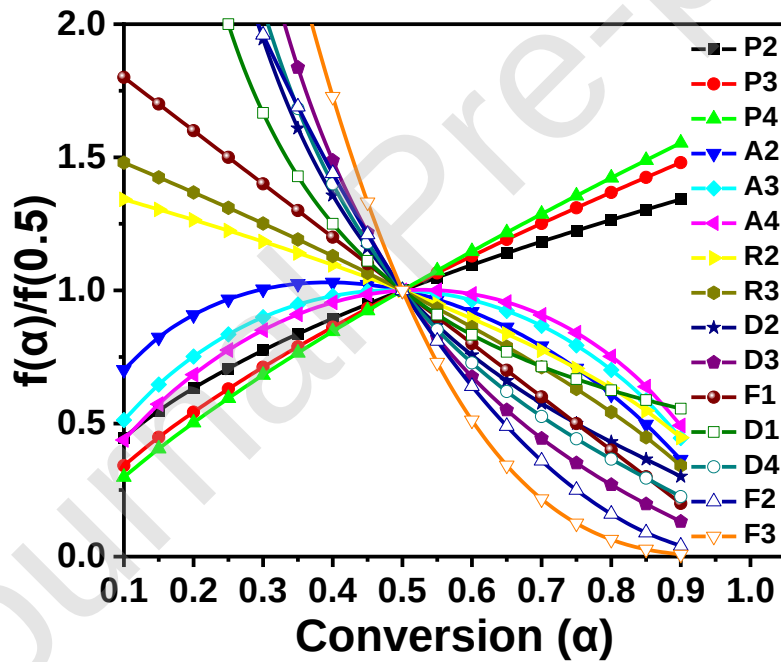


**Figure 8.** Theoretical master plot in differential form representing  $f(\alpha)/f(0.5)$  vs. conversion ( $\alpha$ ) for different solid-state reaction kinetic models presented in Table 4.

To find the suitable rate determining mechanism for our samples, in Fig. 9 we compare the theoretical master plots of  $f(\alpha)/f(0.5)$  with experimental master plots of  $\frac{d\alpha/d\theta}{(d\alpha/d\theta)_{\alpha=0.5}}$  as a

function of  $\alpha$  according to equation (4). From Fig. 9a, the comparative plot for pure AP suggests that the experimental master plot is in good agreement with the D3 reaction model implying that the rate determining mechanism is three-dimensional (3D) diffusion. However, for the AP+1% MA-MgB<sub>2</sub> sample, the data for which is shown in Fig. 9b, the comparative plots suggest that the experimental master plot follows A2 reaction model implying that the rate determining mechanism is two-dimensional (2D) nucleation. This suggests that with the addition of one wt. % of MA-MgB<sub>2</sub> to AP has altered the reaction mechanism by shifting the rate determining step from 3D diffusion to 2D nucleation.

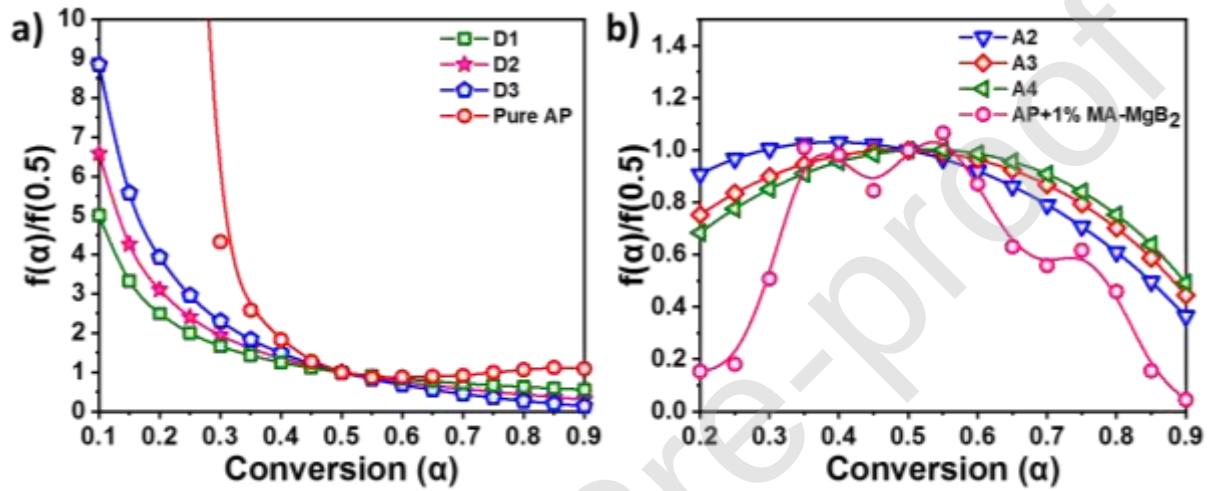


**Figure 9.** Comparison of theoretical master plots with experimental reduced rate data using a generalized kinetic equation of differential form (Eq.4) for: (a) Pure AP, and (b) AP+1% MA-MgB<sub>2</sub>. The experimental reduced rate data are calculated at a constant heating rate of 10 K/min for pure AP and 5 K/min for AP+1% MA-MgB<sub>2</sub> by using the average activation energy values obtained from KAS method. We found that pure AP follows D3 reaction model (Three-Dimensional Diffusion) and AP+1%MA-MgB<sub>2</sub> follows A2 reaction model (Two-Dimensional Nucleation).

By using the observed rate determining reaction mechanism model from master plots and the activation energy values obtained from the KAS method, we have determined the pre-exponential factor (A) at discrete values of conversion using the well-known Coats-Redfern method [43]. The details of the data processing are explained in section 2.8. The values of (A) for pure AP varies from  $\sim 7.50 \times 10^3$  to  $9.56 \times 10^{17} \text{ min}^{-1}$  and for AP+1% MA-MgB<sub>2</sub> it varies from  $\sim 4.67 \times 10^{10}$  to  $9.95 \times 10^{16} \text{ min}^{-1}$ . The linear relationship between the logarithmic form of pre-exponential factor (A) and the activation energy (E) for pure AP and AP+1% MA-MgB<sub>2</sub>

samples are shown in Fig. S9. The linear regression fit shows the value of  $R^2=0.999$  for both the samples indicating that for all the heating rates the value of  $A_a$  is in accordance with the activation energy values at all stages of decomposition process. The range and the average values of activation energy( $E_a$ ), pre-exponential factor (A), and the rate determining mechanism for AP and AP+1% MA-MgB<sub>2</sub> samples are shown in Table 5.

**Table 5.** Kinetic triplets (kinetic parameters ( $E_a$ ,  $A_a$ ) and reaction model) for the thermal decomposition of pure AP and AP with one wt. percentage of MA-MgB<sub>2</sub> composite. Activation energy values obtained using the KAS method and pre-exponential factor obtained using Coats-Redfern method by fitting the reaction models (shown in Table 4) using differential master plots.

| Additive            | $E_a/\text{kJ mol}^{-1}$                   | $A/\text{min}^{-1}$                                                                          | Reaction model |
|---------------------|--------------------------------------------|----------------------------------------------------------------------------------------------|----------------|
| No additive         | Range: $78.62 \pm 6.63 - 248.30 \pm 24.77$ | Range: $7.50 \times 10^3 \pm 0.52 \times 10^2 - 9.56 \times 10^{17} \pm 6.45 \times 10^5$    | D3             |
| MA-MgB <sub>2</sub> | Range: $53.07 \pm 6.26 - 212.82 \pm 8.84$  | Range: $4.67 \times 10^{10} \pm 3.81 \times 10^5 - 9.95 \times 10^{16} \pm 2.06 \times 10^5$ | A2             |

To obtain further insights, we also investigated the decomposition products of AP in the presence of boron-based nanosheets, P-MgB<sub>2</sub>, and MA-MgB<sub>2</sub> using thermogravimetric analysis coupled with mass spectroscopy. Fig. 10a shows the mass loss curve along with the gaseous species evolved during the decomposition of AP. The pure AP on thermal decomposition was found to release H, NH, OH, H<sub>2</sub>O, NH<sub>3</sub>, NH<sub>4</sub>, NO, Cl, HCl, N<sub>2</sub>O, NO<sub>2</sub>, ClO, HOCl, ClO<sub>2</sub>, HClO<sub>2</sub>, Cl<sub>2</sub>, ClO<sub>3</sub>, HClO<sub>3</sub>, and HClO<sub>4</sub> species during LTD and HTD, these matches well with the reported literature [2,6,64]. Mallick et al. did not observe the detection of chloric and perchloric acids and the higher chlorine oxides where as Heath et al. have shown the detection of almost all the species similar to our case shown in Table 6. Only the prominent species are shown in the mass spectra plot in Fig. 10 and all the gaseous species that were detected are listed in Table 6. The NH<sub>4</sub> or H<sub>2</sub>O species curve is not shown in the graph as it is overlapping with the curve of OH or NH<sub>3</sub>. With the addition of one wt. percentage of boron-based nanosheets to AP (Fig. 10b), we observed the release of additional gases B<sub>3</sub>H<sub>2</sub>, BO<sub>2</sub> or B<sub>3</sub>H<sub>10</sub>, and (BO)<sub>2</sub> or B<sub>4</sub>H<sub>10</sub> during the decomposition phases of AP. This suggests that the

boron-based nanosheets releasing  $B_3H_2$ ,  $BO_2$  or  $B_3H_{10}$ , and  $(BO)_2$  or  $B_4H_{10}$  species facilitate the HTD reactions of AP, which was also evident from the TG-DSC analysis shown in Fig. 2, and the additional release of gases is contributing to the increased energy release (as shown in Fig. 3a).

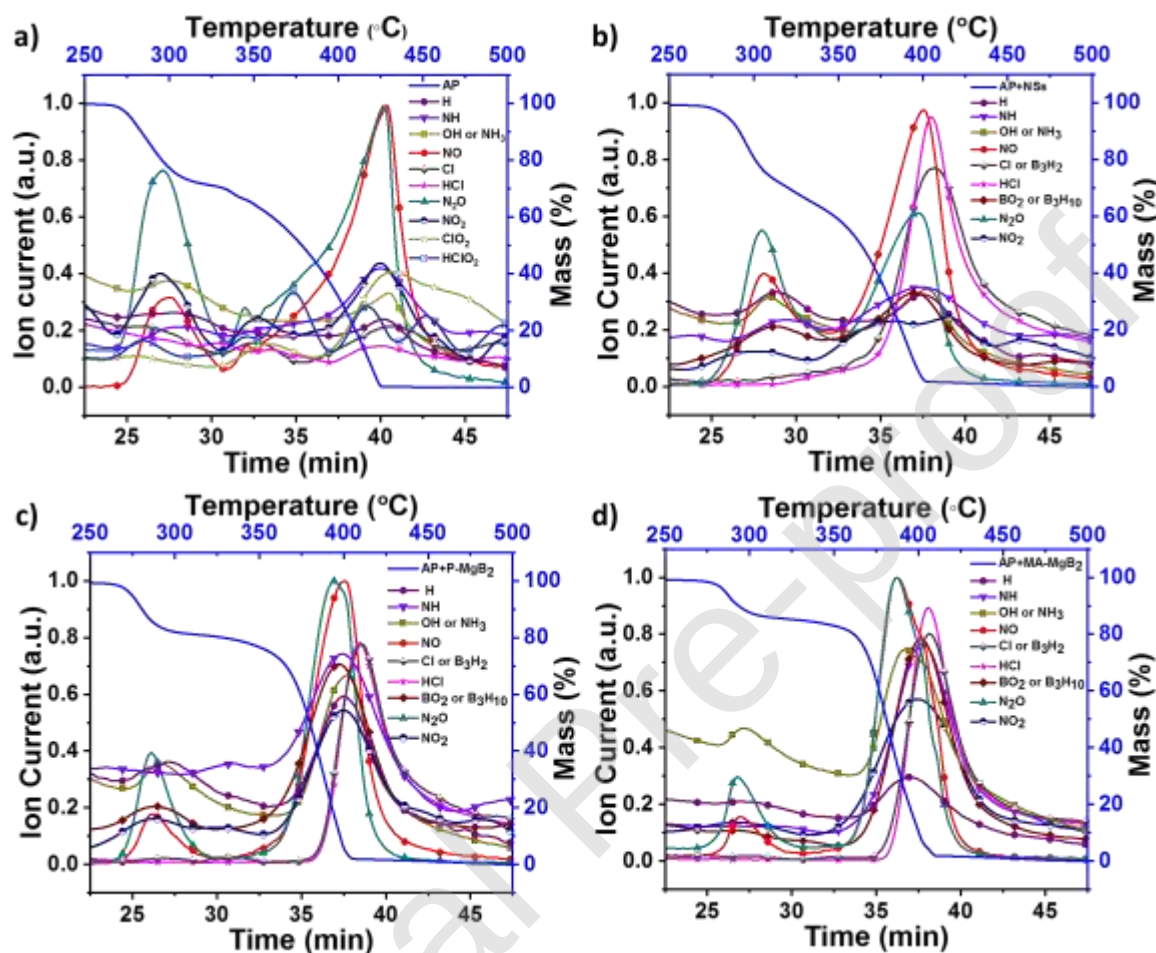


**Figure 10.** TGA-MS signals of evolved gases upon thermal decomposition of AP in the absence and presence of one wt.% of additives derived from LMDB at a heating rate of  $10^{\circ}\text{C min}^{-1}$  — (a) Pure AP or No additive, (b) Nanosheets (NSs), (c) Pristine (P)- $MgB_2$ , and (d) Mechanically Activated (MA)- $MgB_2$  respectively. In the presence of MA- $MgB_2$ , a large number of species were strongly detected indicating, that it favors the decomposition and presence of more active sites enhances the decomposition of AP by promoting the charge transfer or redox reactions of AP at HTD by acting as an electrically conductive surface.

In the case of P- $MgB_2$ /MA- $MgB_2$  as an additive to AP, we also observed the release of additional gaseous species of boranes as well as boron oxides at both LTD and HTD (Fig. 10c and 10d). This indicates that P- $MgB_2$ /MA- $MgB_2$  are not only helping in promoting the charge

transfer or redox reactions of AP during HTD by acting as an electrically conductive surface, but they are also participating in the reaction, which is resulting in the release of boron oxide and boron hydride gases. The evolution of  $\text{BO}_2$  gas was also observed by Liu et al. while testing the effect of magnesium on the burning of boron particles [32]. This indicates that P-MgB<sub>2</sub>/MA-MgB<sub>2</sub> acts as both catalytic and energetic additive in promoting the thermal decomposition of AP, which is also evident from the TG-DSC analysis shown in Fig. 2. The relative intensity of gaseous species detected in the case of MA-MgB<sub>2</sub> is comparatively higher than the case of P-MgB<sub>2</sub>. This promoting effect is attributed to the presence of more active sites or an increase in surface area of the MA-MgB<sub>2</sub>, which was also confirmed through the BET specific surface area analysis (shown in Fig. S8 and Table S6). We found that these are mesoporous in nature and the specific surface area of MA-MgB<sub>2</sub> is found to be double that of P-MgB<sub>2</sub> and also has increased pore volume compared to P-MgB<sub>2</sub>. The effect of the same can also be witnessed from the sharp rise in the HTD peak of AP in the presence of MA-MgB<sub>2</sub>. The profound increment in energy release along with the completion of decomposition at significantly lower temperatures indicates that MA-MgB<sub>2</sub> is a superior catalytic and energetic additive.

**Table 6.** Comparison of evolved species detected in TGA-MS during thermal decomposition of AP in the absence and presence of one wt. % of additives derived from LMDB

| m/z | Species                                             | No Additive | NSs | P-MgB <sub>2</sub> | MA-MgB <sub>2</sub> |
|-----|-----------------------------------------------------|-------------|-----|--------------------|---------------------|
| 1   | H                                                   | ✓           | ✓   | ✓                  | ✓                   |
| 15  | NH                                                  | ✓           | ✓   | ✓                  | ✓                   |
| 17  | OH or NH <sub>3</sub>                               | ✓           | ✓   | ✓                  | ✓                   |
| 18  | H <sub>2</sub> O or NH <sub>4</sub>                 | ✓           | ✓   | ✓                  | ✓                   |
| 30  | NO                                                  | ✓           | ✓   | ✓                  | ✓                   |
| 35  | Cl or B <sub>3</sub> H <sub>2</sub>                 | ✓           | ✓   | ✓                  | ✓                   |
| 36  | HCl                                                 | ✓           | ✓   | ✓                  | ✓                   |
| 43  | BO <sub>2</sub> or B <sub>3</sub> H <sub>10</sub>   | —           | ✓   | ✓                  | ✓                   |
| 44  | N <sub>2</sub> O                                    | ✓           | ✓   | ✓                  | ✓                   |
| 46  | NO <sub>2</sub>                                     | ✓           | ✓   | ✓                  | ✓                   |
| 51  | ClO                                                 | ✓           | ✓   | ✓                  | ✓                   |
| 52  | HOCl                                                | ✓           | ✓   | ✓                  | ✓                   |
| 54  | (BO) <sub>2</sub> or B <sub>4</sub> H <sub>10</sub> | —           | ✓   | ✓                  | ✓                   |

|     |                                |   |   |   |   |
|-----|--------------------------------|---|---|---|---|
| 62  | H <sub>3</sub> BO <sub>3</sub> | — | ✓ | ✓ | ✓ |
| 67  | ClO <sub>2</sub>               | ✓ | ✓ | ✓ | ✓ |
| 68  | HClO <sub>2</sub>              | ✓ | ✓ | ✓ | ✓ |
| 70  | Cl <sub>2</sub>                | ✓ | ✓ | ✓ | ✓ |
| 83  | ClO <sub>3</sub>               | ✓ | ✓ | ✓ | ✓ |
| 84  | HClO <sub>3</sub>              | ✓ | ✓ | ✓ | ✓ |
| 100 | HClO <sub>4</sub>              | ✓ | ✓ | ✓ | ✓ |

The mechanism of AP decomposition in the presence and absence of MA-MgB<sub>2</sub> as a catalytic and energetic additive is explained through a schematic shown in Fig. S10. The presence of MA-MgB<sub>2</sub> does not affect the phase transition temperature and LTD, its effect is pronounced during the HTD reaction of AP. The decomposition mechanism of AP is not clear even today; however, the mechanism proposed by Boldyrev is widely accepted. According to Boldyrev, the initiation of decomposition of AP is through proton transfer mechanism from cation NH<sub>4</sub><sup>+</sup> to anion ClO<sub>4</sub><sup>-</sup>, which form NH<sub>3</sub> and HClO<sub>4</sub>. These intermediate products are partly adsorbed on the surface of AP, which undergo further decomposition and oxidation reactions to form various gaseous species. While some of the intermediate products directly sublime without undergoing further decomposition and oxidation reactions, the intermediate products pile up on the surface of AP at low temperatures and hinder the decomposition reaction, which is why we observe a partial low temperature decomposition peak of AP. At higher temperatures, this closed gaseous layer bursts, which then leads to the complete decomposition of AP. In the case of pure AP, the LTD occurs below 350 °C and HTD occurs above 410 °C and forms various gaseous species, as shown in Fig. S10. In the presence of MA-MgB<sub>2</sub> on the surface of AP, we believe that the MA-MgB<sub>2</sub> acts as a catalytic substrate and helps in the redox reactions by facilitating a charge transfer. This could lead to decomposition at temperatures below 365 °C. This significant shift in the decomposition temperature of AP in the presence of MA-MgB<sub>2</sub> is likely due to the extremely conducting nature of MgB<sub>2</sub>. We also acknowledge that the MA-MgB<sub>2</sub> participates in the reaction forming boron oxides and boron hydride gaseous species, which adds more energy to the overall decomposition reaction of AP. Both these aspects make the MA-MgB<sub>2</sub> a superlative catalytic and energetic additive for fuels.

### 3. Conclusion

We have studied the effect of layered MgB<sub>2</sub> and its derivatives on the thermal decomposition characteristics of AP. The nano derivatives were synthesized by a dissolution recrystallization

method while micro derivatives were obtained by low energy dry ball milling method. With the addition of one wt. percentage of these derivatives to AP, we observed promoting effect in the decomposition of AP. Among boron-based NSs, P-MgB<sub>2</sub>, and MA-MgB<sub>2</sub>, the performance of catalytic and energetic activity is as follows: MA-MgB<sub>2</sub>>P-MgB<sub>2</sub>>boron-based NSs. With the enhanced surface area and mesoporous nature of MA-MgB<sub>2</sub>, we observed an increase in the energy release of AP by 78%, a decrease in the decomposition temperature by ~73°C. The variation of activation energy throughout the decomposition reaction is obtained by following integral model free isoconversional method. The results suggest that the MA-MgB<sub>2</sub> is a promising candidate producing more effect than the nanostructure catalysts fabricated by a sonication process and can be used as a future potential catalytic and energetic additive in tuning the exothermicity of AP. Synthesizing pristine or minimally functionalized MgB<sub>2</sub> nanosheets and utilizing them as additives would further enhance the exothermicity of AP and it would be interesting to see their effect on decomposition characteristics of AP. This study provides a fundamentally new perspective that MgB<sub>2</sub> and its derivatives can be used as catalytic and energetic additives in the field of solid propellants. It would be promising to explore the effect of other members of the MgB<sub>2</sub> family (for example, AlB<sub>2</sub> and TiB<sub>2</sub>) on the exothermicity of solid propellants.

#### Author Statement

**GUNDA HARINI:** Conceptualization, Methodology, Validation, Investigation, Writing-Original Draft, Visualization, and Review & Editing  
**CHINMAY GHOROI:** Resources, Visualization, and Funding Acquisition  
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#### Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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